

Future Development of Liquid Surface Scattering Techniques at APS

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1. Introduction

Synchrotron x-ray scattering is the most powerful probe for *in situ* structural studies at the liquid-gas, liquid-solid and liquid-liquid interfaces. A host of new systems became available for direct structural studies with use of Grazing Incidence X-ray Diffraction (GIXD) and X-ray reflectivity (XR). Areas of scientific interest included Langmuir monolayers, their structure and phase transitions, liquid metal and alloy interfaces, polar and non-polar liquid-liquid interfaces, phospholipid-protein interactions in monolayers, membrane mimetic systems, ultrathin polymer films, supramolecular films, interfaces undergoing mineralization, and, more recently, films of nanoparticles.

2. Present Instrumentation at APS

GIXD and XR on liquids require special multi-axes instrument Liquid Surface Spectrometer (LSS) since the liquid surface is aligned by gravity and cannot be tilted. Therefore the X-ray beam is tilted with respect to the liquid surface by means of a steering crystal while the liquid sample has to be positioned vertically and the scattered beam is mechanically followed with a system of translation and rotation stages. Currently three instruments of the kind exist at APS and are located at Sector 6, Sector 9 and Sector 15. All three instruments have, by and large, similar design and capabilities, and operate in the energy range 4-30 KeV.

3. Future Development

3.1 In order to improve efficiency and satisfy future research needs more advanced and specialized LSS instruments with tunable energy are proposed for the future APS Renewal. Ideally, three specialized LSS instruments would be desirable in the future:

A. "Standard" instrument, similar to the existing ones at APS, capable to hold Langmuir troughs and large vacuum chambers, should be located on a dedicated ID beamline and operate 100% of the time to satisfy current users demands. The instrument should operate energy range from 2 to 30KeV. Extending the lowest accessible energy, with a goal of 2 keV is needed to access light, biologically relevant elements such as P, S, K, Ca using resonant scattering techniques. On the higher energy side, the x-ray energy range of 15 keV to 30 keV allows for the study of certain buried interfaces. These include many liquid-liquid and solid-liquid interfaces.

B. High energy instrument that would operate in the range 30-80 keV to study buried interfaces. The scattering of high energy x-rays from interfaces that are deeply buried within a bulk material is impeded by the x-ray absorption of the bulk. Bulk materials of interest to this community include water, oils, liquid metals, and solid materials such as silicon or minerals that are relevant for the study of solid-liquid interfaces. One example of interest to the study of complex biological interfaces is water, whose absorption length varies from ~0.1 cm at 8 keV to ~5 cm at 60 keV. Other considerations dictate the relatively large path length of x-rays through these samples, from about 2 cm for studies of the solid-liquid interface to 7 cm for studies of the liquid-liquid interfaces. Therefore, higher energy x-rays are a tremendous advantage to the study of these buried interfaces. A new x-ray reflectometer of the kind has been developed at the ESRF. This instrument employs bent Laue crystal optics along with compound lenses to focus the beam to micron size. By

employing two different crystals to tilt the beam downward, this instrument is able to keep the sample height fixed while the incident angle is varied. The estimated users demand for this instrument is 50% of the beamtime.

C. Time-resolved instrument needs to be developed in dispersive mode to perform fast measurements of fragile biological samples as well as the study of some, admittedly slow, time-resolved processes. A range of q -vectors can be measured quickly only by fast-scanning incident optics or by an energy-dispersive measurement using a broad energy spectrum incident beam. In the latter, an effective area detector must be spectroscopic [e.g., 300 eV energy resolution over an energy bandpass of 7–30 keV provides a resolution in q_z of 0.003 Å⁻¹ that is more than adequate] and be able to read out and shift pixel strips on Hz time scales or faster. Energy dispersive schemes might include fast monochromator sweeps (as used for quick-EXAFS), or combinations of mirror and large-bandpass diffractive incident optics, which would need to be developed. Whereas the fast scanning might be possible using a conventional design with an undulator source, an energy-dispersive instrument might require a white beam source. Matsushita at the Photon Factory has had some recent success with millisecond reflectivity curves.

3.2 Time-resolved instruments also dictate development of new area detectors. Traditional CCD detectors are both slow and inefficient at high energies. Some relatively new solid state area detectors, such as Pilatus, suffer from poor resolution and poor sensitivity at high energies. A specialized spectral, pixel detector would need to be developed for the time-resolved measurements. The development of such detectors would be extremely beneficial and generally useful for the x-ray community.

3.3 In a grazing-incidence diffraction measurement, significant scattering from the bulk makes it difficult to use an area detector unless the beam is of micron height. A larger beam spreads over a footprint of 10–100 mm length on the sample surface, and wide angle scattering obtained along this line is overwhelmed by isotropic bulk diffuse scattering. Also, lateral wave-vector resolution suffers if detected rays originate from a long footprint. This is why the present setups typically use Soller slit collimation before a linear detector for wide-angle grazing-incidence diffraction. To make full use of the fast area detectors microbeam focus is required.

3.4 The X-ray scattering experiments could be complemented with x-ray imaging and non-xray in-situ measurements, such as optical microscopy, Brewster angle microscopy, ellipsometry, interferometry, UV-Vis spectroscopy, and others.